which on recrystallization from hexane–benzene afforded 1.10 g (98%) of 5-anilino-1-phenyltetrazole (**26a**): mp 166–167 °C (lit.[22] mp 161 °C); colorless needles; IR 2800–3300, 1610 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 118.6, 122.3, 125.2, 128.8, 129.9, 133.4, 139.9 (aromatic C), 152.5 (C=N); mass spectrum, *m/e* 237 (M^+). Anal. Calcd for $C_{13}H_{11}N_5$: C, 65.81; H, 4.67; N, 29.52. Found: C, 65.82; H, 4.64; N, 29.39.

Similarly, TMSA reacted with *N,N'*-dicyclohexylcarbodiimide (**23b**) or *N,N'*-diisopropylcarbodiimide (**23c**) to afford the corresponding tetrazole, **26b** or **26c**, in 76 or 29% yield, together with recovery of **23b** (24%) or **23c** (56%), respectively.

For **26b**: mp 200–201 °C; colorless needles; IR 3300, 2920, 2840, 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–2.4 (m, 20 H), 3.5–3.85, 3.85–4.3 (each m, 1 H), 4.7–5.05 (br d, NH, *J* = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 25.0, 25.5, 31.9 33.2, 53.7, 55.3 (cyclohexyl C), 154.1 (C=N); mass spectrum, *m/e* 249 (M^+). Anal. Calcd for $C_{13}H_{23}N_5$: C, 62.61; H, 9.30; N, 28.09. Found: C, 62.74; H, 9.39; N, 27.88.

For **26c**: mp 166–167 °C (lit.[21] mp 160–161 °C); colorless needles; IR 3270, 2990, 2950, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31, 1.53 (each d, 6 H, *J* = 6 Hz), 4.07, 4.49 (each double q, 1 H, *J* = 6 Hz), 4.7–5.0 (br, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 21.7, 22.8, 46.5, 48.4 (isopropyl C), 154.2 (C=N); mass spectrum, *m/e* 169 (M^+). Anal. Calcd for $C_7H_{15}N_5$: C, 49.68; H, 8.93; N, 41.39. Found: C, 49.76; H, 8.97; N, 41.24.

Reaction of TMSA with *N*-Cyclohexyl-*N'*-phenylcarbodiimide (23d). A mixture of TMSA (1.3 g, 11.3 mmol) and **23d** (1.12 g, 5.8 mmol) in benzene (2 mL) was stirred at 50–60 °C under nitrogen for 72 h. The reaction mixture was worked up in a similar manner to that described above to give 0.14 g (10%) of 5-cyclohexylamino)-1-phenyltetrazole (**26d**), together with recovery of **23d** (0.95 g, 85%). Similarly, TMSA reacted with *N*-*n*-butyl-*N'*-phenylcarbodiimide (**23e**) to afford 5-(*n*-butylamino)-1-phenyltetrazole (**26e**) in 10% yield, together with recovery of **23e** (89%).

For **26d**: mp 121–122 °C (lit.[23] mp 120.5–121.5 C); colorless needles; IR 3220, 2930, 2850, 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–2.5 (m, 10 H), 3.6–4.1 (m, 1 H), 4.2–4.6 (br d, 1 H, NH, *J* = 7 Hz), 7.4–7.9 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 24.8, 25.4, 33.2, 53.5 (cyclohexyl C), 123.9, 124.9, 129.1, 129.7, 130.3, 133.3 (aromatic C), 153.9 (C=N); mass spectrum, *m/e* 243 (M^+). Anal. Calcd for $C_{13}H_{17}N_5$: C, 64.17; H, 7.04; N, 28.79. Found: C, 64.46; H, 7.04; N, 28.61.

For **26e**: mp 104–105 °C; colorless needles; IR 3230, 2950, 2930, 2860, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (t, 3 H, *J* = 6 Hz), 1.1–2.0 (m, 4 H), 3.48 (dt, 2 H, *J* = 5, 6 Hz), 4.7–5.1 (br t, 1 H, NH, *J* = 5 Hz), 7.4–7.8 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 13.7, 19.9, 31.5, 44.2 (butyl C), 123.8, 129.5, 130.0, 133.2 (aromatic C), 154.7 (C=N); mass spectrum, *m/e* 217 (M^+). Anal. Calcd for $C_{11}H_{15}N_5$: C, 60.80; H, 6.96; N, 32.24. Found: C, 60.66; H, 7.05; N, 31.94.

Reaction of TMSA with Diphenylketene (27). (i) A solution of TMSA (1.5 g, 13 mmol) and azibenzil (2.85 g, 12.8 mmol) in benzene (15 mL) was refluxed for 6 h. The reaction mixture was concentrated in vacuo, and the residue was chromatographed on silica gel with benzene and chloroform as eluents. From benzene elution, 0.34 g (13%) of *N*-(diphenylacetyl)tetraphenylsuccinimide (**29**) and 40 mg (2%) of 1,3-bis(diphenylmethyl)urea (**30**) were obtained, and the chloroform elution gave 1.28 g (50%) of tetraphenylsuccinimide (**28**) together with diphenylacetic acid (80 mg).

For **28**: mp 261–262 °C (lit.[25] mp 256–258 °C); colorless prisms; IR 3240, 1775, 1725, 1710 cm^{-1}; ^{13}C NMR (Me_2SO-d_6) δ 68.8 (quaternary C), 126.8, 127.2, 130.2, 139.5 (aromatic C), 177.5 (C=O); mass spectrum, *m/e* 403 (M^+). Anal. Calcd for $C_{28}H_{21}NO_2$: C, 83.35; H, 5.25; N, 3.47. Found: C, 83.10; H, 5.28; N, 3.34.

For **29**: mp 206–207 °C; colorless needles; IR 1800, 1750, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.94 (s, 1 H), 7.0–7.35 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 59.2 (tertiary C), 68.4 (quaternary C), 127.2, 127.4, 128.7, 128.7, 130.7, 136.1, 138.5 (aromatic C), 171.6, 174.3 (C=O); mass spectrum, *m/e* 597 (M^+). Anal. Calcd for $C_{42}H_{31}NO_3$: C, 84.40; H, 5.23; N, 2.34. Found: C, 84.30; H, 5.26; N, 2.46.

For **30**: mp 278–279 °C; colorless needles; IR 3320, 1630 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 5.94 (d, 2 H, *J* = 8 Hz), 7.0 (d, 2 H, NH, *J* = 8 Hz), 7.2–7.5 (m, 20 H); ^{13}C NMR (Me_2SO-d_6) δ 56.9 (tertiary C), 126.7, 128.2, 143.4 (aromatic C), 156.2 (C=O); mass spectrum, *m/e* 392 (M^+). Anal. Calcd for $C_{27}H_{24}N_2O$: C, 82.62; H, 6.16; N, 7.14. Found: C, 82.54; H, 6.17; N, 7.02.

(ii) TMSA (1.5 g, 13 mmol) was added to a solution of **27**, generated in situ from azibenzil (2.85 g, 12.8 mmol), in benzene (15 mL) at room temperature. After the reaction mixture was stirred at room temperature for 6 h, a workup similar to that above gave **28** (0.59 g, 23%), **29** (0.46 g, 18%), and **30** (15 mg, 0.6%).

(iii) TMSA (3.0 g, 26 mmol) was added to a solution of **27**, generated in situ from azibenzil (2.85 g, 12.8 mmol), in xylene (15 mL) at −4 °C for 3 h, and then the reaction mixture was allowed to stand overnight at room temperature. A workup of the reaction mixture similar to that above afforded 0.26 g (10%) of **28** and 0.32 g (11%) of benziloylamide (**31**), mp 154–156 °C (lit.[28] mp 154–155 °C).

Registry No. **1a**, 103-71-9; **1b**, 5416-93-3; **1c**, 104-12-1; **1d**, 100-28-7; **3a**, 940-38-5; **6a**, 5097-82-5; **6b**, 62442-51-7; **6c**, 3589-06-8; **6d**, 75430-97-6; **7a**, 75430-98-7; **8a**, 4461-33-0; **8b**, 4695-57-2; **8c**, 4461-36-3; **9a**, 3553-61-5; **9b**, 3553-62-6; **9c**, 3553-63-7; **12c**, 75430-99-8; **13a**, 21084-84-4; **13b**, 75431-00-4; **13c**, 21084-85-5; **14a**, 5378-17-6; **14b**, 75431-01-5; **14c**, 75444-53-0; **16**, 103-72-0; **17**, 532-55-8; **21**, 13078-30-3; **22**, 15150-25-1; **23a**, 622-16-2; **23b**, 538-75-0; **23c**, 693-13-0; **23d**, 3878-67-9; **23e**, 21848-95-3; **25a**, 75431-02-6; **26a**, 64287-36-1; **26b**, 73565-25-0; **26c**, 75431-03-7; **26d**, 66907-71-9; **27**, 525-06-4; **28**, 22270-82-2; **29**, 75431-04-8; **30**, 6744-64-5; **31**, 4746-87-6; TMSA, 4648-54-8; 2-phenylthiazoline-4,5-dione, 1628-53-1.

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Crystal Structure of 1,3,5-Trithiane 1-Oxide

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The conformation of 1,3,5-trithiane 1-oxide (**3**) observed in the crystal, as determined by single-crystal X-ray diffraction, has the sulfoxide oxygen axial. Previous studies involving proton and carbon nuclear magnetic resonance spectroscopy, as well as molecular mechanics calculations, indicated that the equatorial oxide is highly preferred in solution. Close C–H···O and S···O intermolecular contacts in the solid suggest that crystal packing is sufficiently strong to overcome the electrostatic destabilization of the axial conformation of **3**. Crystals of **3** conform to space group *Pnma* (D_{2h}^{16}, No. 62) with *a* = 19.179 (9), *b* = 7.044 (4), *c* = 4.629 (3) Å and *Z* = 4. The crystal structure was determined by the Patterson method. Least-squares refinement gave *R* = 0.046 for 833 reflections (493 independent data) whose intensities were measured by counter diffractometry using Cu Kα radiation.

Introduction

The conformational properties of six-membered cyclic sulfoxides have been examined by a variety of experimental techniques with most of the recent emphasis centered on nuclear magnetic resonance spectroscopy (both proton[1] and carbon[2] NMR) and X-ray crystallography.[3]

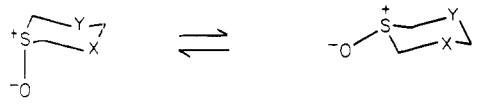
0022-3263/80/1945-5136$01.00/0

Table I. Atomic Parameters Defining the Crystal Structure of 1,3,5-Trithiane 1-Oxide[a]

atom	x	y	z	B	r_1	r_2	r_3
S(1)	346 (1)	2500 (-)	2218 (3)	2.31	140	159	207
S(3)	1694 (1)	4653 (2)	1080 (2)	3.00	142	205	228
O	283 (2)	2500 (-)	-1019 (7)	2.88	135	200	227
C(2)	920 (2)	4440 (5)	3229 (8)	2.93	138	204	225
C(4)	2119 (3)	2500 (-)	2099 (13)	3.46	183	210	233
H(2a)	630	5749	3044	5.0			
H(2b)	1075	4232	5449	5.0			
H(4a)	2170	2500	4423	5.0			
H(4b)	2631	2500	1127	5.0			

[a] Positional parameters are given as fractions of the unit cell edges (× 10^4) and equivalent isotropic B values are given in Å² together with the root-mean-square amplitudes of vibration along the principal axes of the thermal ellipsoids (Å × 10^3). Standard deviations are given in parentheses and are applicable to the least significant digits.

The energies of individual conformers of a number of cyclic sulfoxides of this type have been calculated, using molecular mechanics methods, and subjected to a thorough analysis.[4] Theory and experiment agree that while the axial oxide is slightly more stable than the equatorial for the case of thiane 1-oxide (1),[5] the equatorial oxide is more stable than the axial in 1,3-dithiane 1-oxide (2).[1] The significance of destabilizing electrostatic interactions between an axial sulfoxide oxygen and the cross-ring sulfur in 2 have been discussed in both qualitative[1,6] and quantitative[4] terms. The conformational situation in 2 appears to be yet another manifestation of a general phenomenon in which anti S–A–B–O arrays have been observed to be more stable than gauche forms.[7]



1, X = Y = CH_2 ΔG° = +0.17 to 1.3 kcal/mol
2, X = S; Y = CH_2 ΔG° = -0.6 kcal/mol
3, X = Y = S

Dynamic ^1H NMR studies of 1,3,5-trithiane 1-oxide (3) revealed a strong conformational bias so that only a single conformation could be detected at -70 °C.[1b] By analogy to 2, it was suggested that the observed conformation was the equatorial oxide. The calculations of Allinger and Kao indicate that the equatorial conformation of 3 is 3.5 kcal/mol more stable than the axial (for a dielectric constant of 1.0). Subsequently, a ^{13}C NMR study revealed a pattern of chemical shifts for 3 which were completely consistent with an equatorial orientation of the sulfoxide oxygen.[2] Thus, there seems little reason to doubt that 3 exists in solution in the equatorial oxide conformation.

Since X-ray crystallographic structure determinations have played a major part in clarifying stereochemical relationships in 2 and its derivatives,[3] we undertook to obtain similar information in the trithiane system.

Table II. Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) of 1,3,5-Trithiane and its 1-Oxide[a]

	1,3,5-trithiane[b]	1,3,5-trithiane 1-oxide (3)
bond lengths		
S(1)-C(2)	1.824 (6)	1.816 (3)
C(2)-S(3)	1.813 (7)	1.794 (3)
S(3)-C(4)	1.816 (3)	1.785 (2)
S(1)-O		1.503 (2)
bond angles		
S(1)-C(2)-S(3)	115.1 (4)	115.0 (2)
C(2)-S(3)-C(4)	100.7 (5)	99.2 (2)
S(3)-C(4)-S(5)	115.3 (4)	116.3 (3)
C(6)-S(1)-C(2)	99.2 (6)	97.6 (2)
O-S(1)-C(2)		107.8 (2)
torsion angles		
S(1)-C(2)-S(3)-C(4)		-66.1
C(2)-S(3)-C(4)-S(5)		65.0
S(5)-C(6)-S(1)-C(2)		-66.9

[a] Estimated standard deviations are given in parentheses. [b] Taken from ref 8.

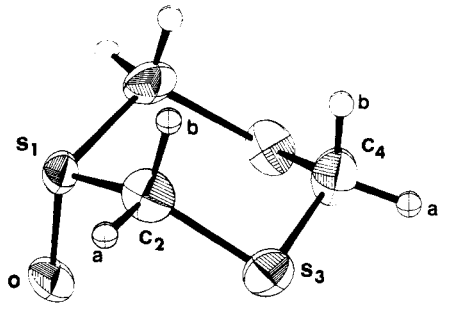


Figure 1. ORTEP drawing of the structure of 3. Thermal ellipsoids for S, O, and C are drawn with the 50% probability level as boundary surface. Hydrogen atoms, where located, are represented by spheres of arbitrary radius.

Results and Discussion

The atomic parameters which define the crystal structure of 1,3,5-trithiane 1-oxide (3) are presented in Table I; bond lengths, bond angles, and torsion angles are given in Table II which also includes for comparison purposes structural parameters taken from the literature[8] for the parent compound 1,3,5-trithiane. Figure 1 shows an ORTEP[9] drawing of 3. By crystallographic requirements the molecule has a mirror plane of symmetry passing through S(1) and C(4). Atoms related by the mirror plane are given the same number and are distinguished as primed and unprimed.

Surprisingly, and in contrast to the solution behavior of 3 inferred from ^1H and ^{13}C NMR data and the results of molecular mechanics calculations, the conformation of 3 adopted in the crystal has the sulfoxide oxygen axial. The conformation is a puckered chair in which the sum of the ring torsion angles is 396° (the corresponding value

(1) See, for example, for 1,3-dithiane 1-oxide and derivatives: (a) Van Acker, L.; Anteunis, M. *Tetrahedron Lett.* **1974**, 225–228; (b) Khan, S. A.; Lambert, J. B.; Hernandez, O.; Carey, F. A. *J. Am. Chem. Soc.* **1975**, *97*, 1468–1473; (c) Cook, M. J.; Tonge, A. P. *J. Chem. Soc., Perkin Trans. 2* **1974**, 767–772; (d) Bergesen, K.; Cook, M. J.; Tonge, A. P. *Acta Chem. Scand., Ser. A* **1976**, *30*, 574–576.

(2) Carey, F. A.; Dailey, O. D., Jr.; Hutton, W. C. *J. Org. Chem.* **1978**, *43*, 96–101 and references cited therein.

(3) (a) McPhail, A. T.; Onan, K. D.; Koskimies, J. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1004–1008. (b) Bryan, R. F.; Carey, F. A.; Miller, R. W. *J. Org. Chem.* **1979**, *44*, 1540–1543.

(4) Allinger, N. L.; Kao, J. *Tetrahedron*, **1976**, *32*, 529–536.

(5) (a) Johnson, C. R.; McCants, D., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 1109–1114; (b) *ibid.* **1964**, *86*, 2935–2936. (c) Martin, J. C.; Uebel, J. J. *J. Am. Chem. Soc.* **1964**, *86*, 2936–2937. (d) Lambert, J. B.; Keske, R. G. *J. Org. Chem.* **1966**, *31*, 3429–3431.

(6) Carey, F. A.; Smith, P. M.; Maher, R. J.; Bryan, R. F. *J. Org. Chem.* **1977**, *42*, 961–967.

(7) Eliel, E. L.; Juaristi, E. *J. Am. Chem. Soc.* **1978**, *100*, 6114–6119.

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(9) Johnson, C. K. "ORTEP-II. A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, ORNL-5138", Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

for cyclohexane is 335°). The S(1)–C(2)–S(3) angle of **3** (115.0°) is slightly smaller than the S(3)–C(4)–S(3′) angle (116.3°) and almost identical with the S–C–S angle of 1,3,5-trithiane itself (115.1°). This insensitivity of the S–C–S angle to the presence of an oxide substituent on sulfur stands in contrast to the behavior of 2-phenyl-1,3-dithiane 1-oxides observed earlier.[6] There, the S(1)–C(2)–S(3) angle decreased from 115° in the parent dithiane to 112.8° in the axial oxide and 109.6° in the equatorial oxide. The different behavior of 1,3,5-trithiane on conversion to its axial 1-oxide may be rationalized by noting that any contraction of the S(1)–C(2)–S(3) and, by symmetry, the S(1)–C(2′)–S(3′) angles is accompanied by contraction of the S(3)–C(4)–S(3′) angle. Contracting the S(3)–C(4)–S(3′) angle decreases the S(3)···S(3′) separation and is opposed by electron–electron repulsions between S(3) and S(3′). The S(3)···S(3′) separation is already slightly smaller (3.032 Å) in **3** than in 1,3,5-trithiane (3.068 Å) even though the angle at C(4) is somewhat larger. The reason for this apparent anomaly is that the bond lengths in **3** are generally shorter than those in 1,3,5-trithiane.

Other structural features of **3** parallel those already observed in 1,3-dithiane 1-oxides. The sulfur–carbon bond distances involving the sulfoxide sulfur are longer (1.816 Å) than those involving the other two sulfur atoms: the S(3)–C(2) distance is 1.794 Å and S(3)–C(4) is 1.785 Å. Related instances of bond elongation in 1,3-dithiane 1-oxides have been attributed to gauche repulsions between the sulfoxide group and the C(2) substituents.[3] The S(1)–C(2) distance in **3** is similar to that of 1,4-dithiane *trans*-1,4-dioxide (1.81 Å).[10]

In previous studies two factors emerged as significant influences on conformational equilibria in oxides of 1,3-dithiane: (1) electrostatic interactions between the sulfoxide group and the cross-ring sulfur favor an equatorial orientation of oxygen; (2) gauche interactions between the sulfoxide group and C(2) and C(6) may favor an axial orientation of oxygen but are usually attenuated by C–S bond stretching; only when C(2) is disubstituted with conformationally demanding substituents do gauche interactions dominate over electrostatic interactions. These two considerations apply as well to the conformational analysis of **3**, but we see that the presence of a third sulfur in the ring introduces a new feature. The electrostatic attraction between an equatorial sulfoxide and the cross-ring sulfur is opposed in **3** by an increased electron–electron repulsion between S(3) and S(3′). As stated earlier, both theory and experiment indicate that the preferred conformation of **3** has the oxygen equatorial so the S(3)···S(3′) interaction is probably less important than the interactions of the sulfoxide group with S(3) and S(3′). We are therefore led to ascribe the axial oxide conformation observed in the solid phase of **3** to crystal packing.

The molecular packing of **3** in the crystal, depicted in Figures 2 and 3, reveals a pattern of short O···H and O···S contacts between an individual molecule and four neighbors. In particular, the sulfoxide oxygen is flanked by the C(2) equatorial hydrogens of two adjacent molecules at a distance of 2.34 Å. Further, its own C(2) and C(2′) equatorial hydrogens are involved in corresponding close contacts with the axial oxygens of these two neighbors. The result is a highly ordered arrangement in a direction perpendicular to the symmetry plane of the molecule. The 2.34 Å O···H separation is less than the sum of their van der Waals radii (2.6 Å).[11] Molecules of **3** stack on top of

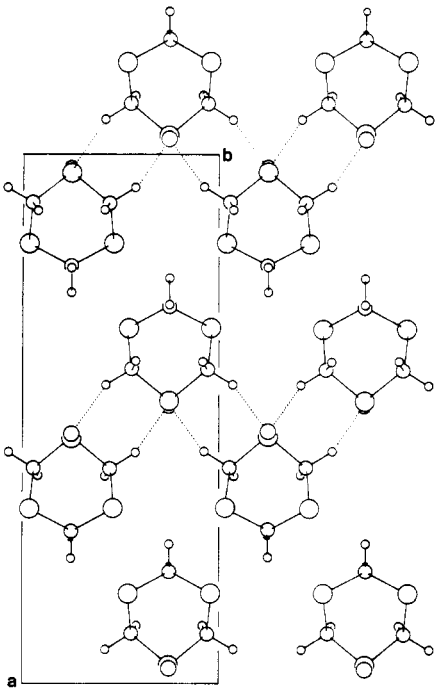

Figure 2. View in *c*-axis projection of the molecular packing in **3**.

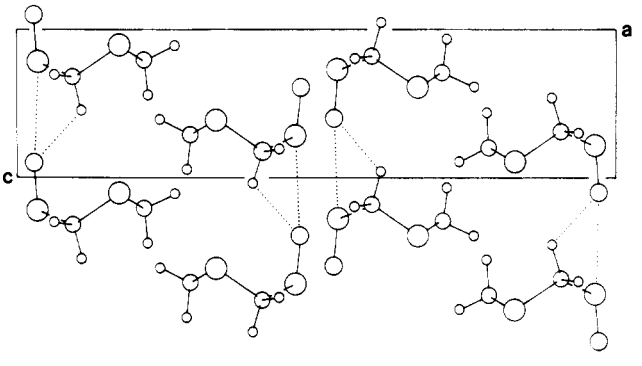

Figure 3. View in *b*-axis projection of the molecular packing in **3**.

each other so that their symmetry planes coincide and with an oxygen of one sulfoxide 3.13 Å from the sulfoxide sulfur of another (Figure 3). Again, this contact is closer than the sum of the van der Waals radii of oxygen and sulfur (3.25 Å).[11] Taken in sum, these O···H and S···O interactions may provide sufficient stabilization of the axial oxide to overcome its calculated 3.5 kcal/mol greater energy than that of the equatorial oxide conformation. Direct comparison of the solution and solid-state structures of **3** by infrared spectroscopy is inconclusive. The spectra in chloroform solution and in potassium bromide are similar and an early systematic study of cyclic sulfoxides concluded with the statement that a reliable conformational analysis of **3** was not possible on the basis of the infrared data then available.[12]

If, as seems likely, the dominant conformation of **3** in solution has the oxygen equatorial, these results offer an example of a striking dependence of conformation on physical state. Precedents for differences in conformational preference of this magnitude between solution and the solid phase are difficult to find in the literature although the relationship between solid-state and solution

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(12) Cairns, T.; Eglinton, G.; Gibson, D. T. *Spectrochim. Acta* **1964**, *20*, 159–167.

conformation has long been a source of concern, especially to protein crystallographers. Among small molecules, it has been found that the antibiotic cycloheximide incorporates both chair and twist-boat conformations of its 2,4-dimethylcyclohexanone moiety into the same crystal.[13] These conformations are estimated to differ by 2–3 kcal/mol and both may be populated in solution although evidence is not yet available on this point. Some steroids with aromatic A rings, such as 2,4-dibromoestradiol,[14] crystallize in two forms which differ in the conformation of the B ring, but in these cases the energy difference between conformations is quite small.[15] We view the conformational situation in **3** as a special case in which the molecular symmetry, substantial dipole moment, and potential for intermolecular interactions both in the symmetry plane of the molecule and perpendicular to it permit efficient packing of the axial conformation despite its increased energy.

Experimental Section

1,3,5-Trithiane 1-oxide (**3**), available from previous work,[1b] was crystallized slowly from dimethyl sulfoxide to give crystals suitable for X-ray diffraction.

X-ray Crystallographic Measurements, Crystal Data. The unit-cell symmetry was established from 25° precession photographs taken with Mo Kα radiation. The crystal system is orthorhombic, and systematic absences $0kl$ with $k + l$ odd and $hk0$ with h odd are compatible with space groups $Pnma$ (D_{2h}^{16}, No. 62) or $Pn2_1a$ (C_{2v}^{9}, No. 33, $b \rightleftarrows c$). The former group was chosen on the basis of the distribution of maxima in the Patterson function and, with only four molecules in the unit cell, requires that each molecule have mirror symmetry. Accurate unit-cell dimensions were derived from a least-squares fit to the observed values of $\pm 2\theta$ for 12 strong general reflections, measured from a crystal carefully centered on the diffractometer. They are as follows: a = 19.179 (9), b = 7.044 (4), and c = 4.629 (3) Å for λ = 1.5418 Å. For Z = 4, the calculated density is 1.638 g cm^{-3}. That observed by flotation in an ethyl iodide–hexane mixture is 1.65 g cm^{-3}. $F(000)$ is 320 and the absorption coefficient, μ, for Cu Kα radiation is 95 cm^{-1}. No absorption correction was made and most of the residual errors are attributable to this neglect.

Intensity Data. Measurements of intensity were made from a single-crystal prism 0.2 mm on a side and mounted with c^* parallel to the ϕ-axis of a Picker four-circle diffractometer operated under the control of an XDS Sigma 2 computer. Cu Kα radiation was used, made monochromatic by Bragg reflection of the direct beam from a highly oriented graphite crystal. Two symmetry-equivalent octants of reciprocal space, hkl and $\bar{h}kl$, were surveyed to 2θ = 120°. Intensity significantly above background [$I > 3\sigma(I)$] was measured at 833 of the 986 accessible reflections (493 independent data). Scintillation counting was used with pulse height analysis. The θ–2θ scan technique was used with a scan range of 4° and a scan speed of 2° min^{-1} in 2θ. Background measurements were made for 10 s at the beginning and end of each scan with both crystal and counter at rest. Stability of the experimental conditions was monitored by measurement of the intensity of two symmetry-equivalent reflections after every 50 scans. With a mean intensity of about 25 000 counts, the root-mean-square deviations of individual reflections from the mean were 1.1% in each case. Structure amplitudes were derived in the usual ways. The residual between the two sets of symmetry-equivalent data is 3.6%. Both octants were used in the later refinement.

Structure Determination and Refinement. The positions of the two independent sulfur atoms were derived from a three-dimensional Patterson function and the structure solved by the heavy-atom method. Block-diagonal least-squares refinement gave R = 0.12 when individual isotropic thermal parameters were used and R = 0.055 when anisotropic thermal parameters were used for S, O, and C. A conventional weighting scheme was used.[17] Hydrogen atoms were located from a three-dimensional difference electron-density map and their parameters included in the least-squares process. The refinement gave physically unreasonable parameters for the hydrogen atoms, however, and so fixed contributions for these atoms were taken instead, based on C–H distances of 1.08 Å and isotropic B values of 5.0 Å^2. At convergence [$\Delta(p) < 0.1\sigma(p)$] the usual unweighted and weighted residuals were 0.046 and 0.052. A final difference electron-density map showed residual peaks (±0.57 e/Å^3) close to the sulfur positions, most probably attributable to neglect of absorption corrections, but was otherwise structurally featureless. The scattering functions were taken from ref 16. All programs used were written in this laboratory for the XDS Sigma 2 computer, with the exception of ORTEP for which a CDC Cyber 172 computer was used.

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Supplementary Material Available: Listing of anisotropic thermal parameters (1 page). Ordering information is given on any current masthead page.

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Quinone Chemistry. Reaction of 2,3-Dichloro-1,4-naphthoquinone with Arylamines in Pyridine

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2,3-Dichloro-1,4-naphthoquinone (**1**) reacts with arylamines (**2**) in pyridine to afford 2-(arylamino)-3-chloro-1,4-naphthoquinone (**6**), 2-(arylamino)-1,4-naphthoquinone (**5**), 2-(arylamino)-1,4-naphthoquinone-3-pyridinium perchlorate (**4**), and 2-amino-1,4-naphthoquinone-3-pyridinium perchlorate (**7**), depending upon the nature of the substituent in **2**. 2-(4-Nitroanilino)-1,4-naphthoquinone-3-pyridinium chloride (**4e**, X = Cl) reacts with alkali to give 1-oxo-2-(4-nitrophenylimino)-3-pyridinium-4-naphthoxide (**9**), not the product reported[12] previously. Intermediate compounds have been isolated and characterized. A probable mechanism for the formation of the derivatives is discussed.

In continuation of our interest in quinone chemistry, we have synthesized indazolequinones,[1] benzoisoxazole-quinones,[2] quinazoline-5,8-quinones,[3,4] acridinequinones,[5] 2-(alkylamino)-5-(arylamino)-1,4-benzoquinones,[6] amino-

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